REFRACTORY AND HARD MATERIALS IN THE Ti-Si-B-C-N SYSTEM – PHASE EQUILIBRIA, PHASE REACTIONS AND THERMAL STABILITIES

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ABSTRACT

A thermodynamic dataset was developed for the quinary Ti-Si-B-C-N system. The phase modeling includes all carbides, nitrides, carbonitrides, borides and silicdes which can be used as high temperature structural materials. The CALPHAD approach is used to calculate high-temperature phase reactions in the ternary and quaternary subsystems. The phase stabilities can be derived. All types of phase diagrams, phase fraction diagrams and phase composition diagrams are used to simulate the microstructure development of the multicomponent-multiphase materials. This approach can be used to predict the materials behavior at high temperatures.

1. INTRODUCTION

The quinary Ti-Si-B-C-N system includes numerous stoichiometric and solid solution carbides, nitrides, and borides which are of high interest as high temperature structural materials for military applications. In the binary subsystems mainly the phases α-/β-SiC, α-/β-/c-Si$_3$N$_4$, B$_{4+x}$C, α-/β-/γ-BN, TiC$_{1-x}$, TiN$_{1-x}$, SiB$_3$, SiB$_6$ and SiB$_n$, are of interest. Additionally, some of the Ti-silicides are commercially useful for high temperature electronic and structural use, e.g. Ti$_5$Si$_3$ and TiSi$_2$. The ternary systems include the solid solution series TiC$_x$N$_{1-x}$, the Nowotny phase Ti$_5$Si$_3$(B,C)$_{1-x}$ and the compounds β-SiC$_2$N$_4$ and Si$_2$CN$_4$. The complex carbide Ti$_3$SiC$_2$ with unique mechanical (high temperature) properties is currently under intensive investigation. Recently, a new ternary compound Ti$_6$Si$_2$B was reported to be stable in the Ti-Si-B system. Also, numerous metastable binary and ternary compounds are known. To understand the phase reactions and the high temperature materials stabilities in the five-component system, 25 subsystems have to be explored: The quinary system includes 10 binary, 10 ternary and 5 quaternary subsystems.

The materials reaction behaviors in such a complex system have to be investigated efficiently by a combined approach including thermodynamic simulations (CALPHAD approach, CALculation of PHAse Diagrams) [1] and carefully selected experiments. Only very few investigations on materials reactions in the Ti-containing quaternary systems Ti-Si-B-C, Ti-Si-B-N, Ti-Si-C-N and Ti-B-C-N are published, whereas the Si-B-C-N system has been investigated in detail [2].

A manifold of synthesis and processing methods are applied to produce bulk materials, composites and coatings in this five component system. For example, the synthesis from precursor polymers is a novel way to produce materials for high temperature use. Novel ceramics with high temperature stability and with good resistance against oxidation can be obtained from molecular units without sintering aids. For some applications, such as coating or fiber preparation, the precursor route is also the practical way. Multicomponent-multiphase materials in the system are also produced by hot pressing, reaction sintering or self-propagating high temperature synthesis (SHS). To understand the materials processing in detail, the underlying phase equilibria and reactions have to be known in detail.

The main goal of this work was to study the thermal stability with respect to the phase equilibria and the phase reactions of ceramics and refractory and hard materials in the Ti-Si-B-C-N system by means of CALPHAD, high temperature experiments and in-situ or subsequent materials analysis by DTA/TG, XRD, SEM and TEM. Based on earlier work for the Ti-Si-C system [3] and the Si-B-C-N system [2], a consistent thermodynamic dataset for the Ti-Si-B-C-N system was developed. For the analytical descriptions of the phases, guidelines were taken into account, which were developed during a series of workshops on thermodynamic modeling and application [4-7]. Thermodynamic calculations of different types of phase diagrams, phase fraction diagrams and phase composition diagrams in regard to the reaction behavior of the high temperature materials were carried out using software such as BINGSS/BINFKT [8] and THERMO-CALC [9]. DTA was combined with TG to investigate the phase reactions and the thermal stability of materials in the Ti-Si-B-C-N system. The materials were characterized up to temperatures of 2500°C. The microstructures and the phase compositions of the materials and the heat treated products were analyzed in detail. Thermal stability has been recognized as a key aspect with respect to the development and application of

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ceramics and hard materials. Since the finding of high temperature stability of precursor-derived Si-B-C-N ceramics up to 2000°C, understanding of these phenomena has been scarcely developed.

An overview on the ternary and quaternary thermodynamic datasets and calculations in the systems is given below.
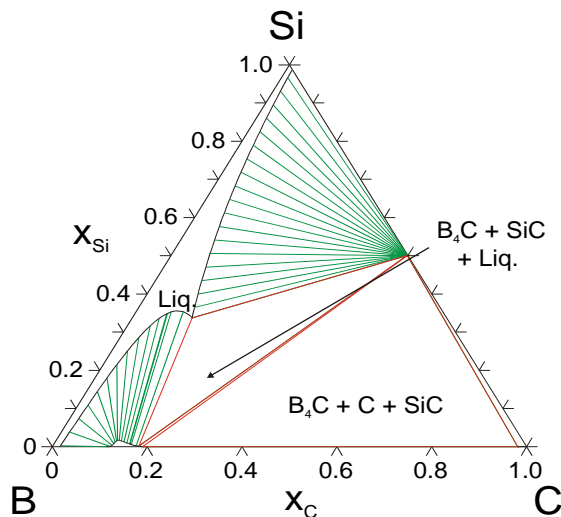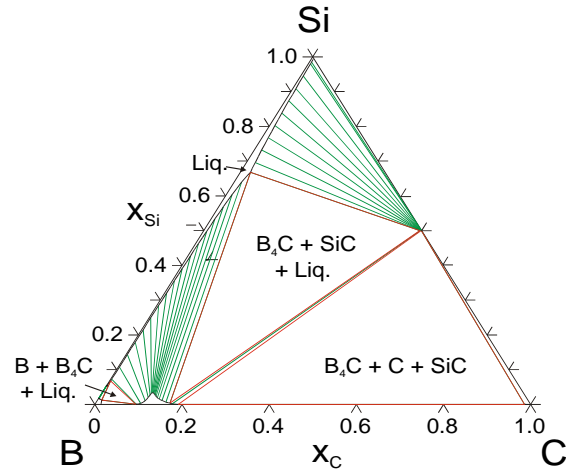
2. TERNARY SYSTEMS

2.1 Si-B-C System

The ternary thermodynamic dataset was used to calculate isothermal sections (Fig. 1). The ternary solubility of boron carbide was taken into account. The comparison of the diagrams for temperatures of 2600 and 2500 K illustrate the transition reaction $L + C = B_{4+\delta}C + SiC$ which occurs at a calculated temperature of 2568 K.
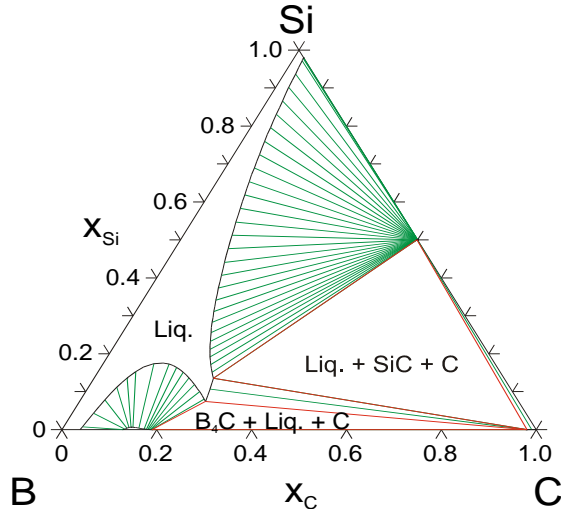
c) 2323 K

a) 2600 K
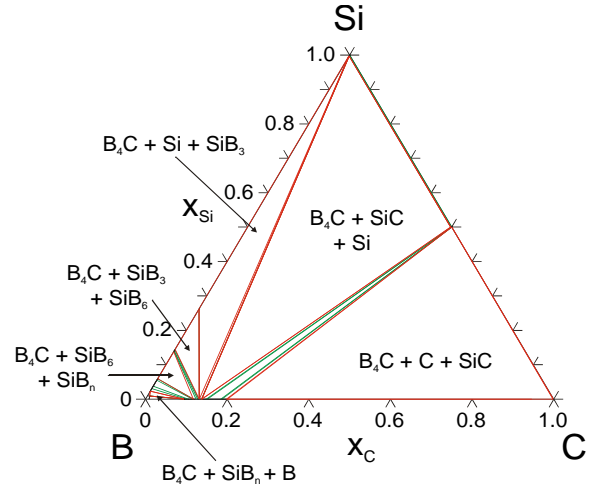
d) 1400 K

Fig. 1. Calculated isothermal sections in the Si-B-C system.

2.2 Si-B-N System

The Si-B-N system can be calculated from the binary subsystems without using ternary parameters.

2.3 Si-C-N System

The thermal degradation of precursor-derived Si-C-N ceramics has been characterized quantitatively by taking into account the endothermic phase reactions $Si_3N_4 + 3C = 3SiC + 2N_2$ (1484°C) and $Si_3N_4 = 3Si + 2N_2$ (1841°C) [10]. Fig. 2 shows the thermal analysis (TGA) of a precursor ceramics of composition (38.2 Si, 22.9 C, 38.9 N; at.%), derived from a polyhydridomethylsilazane (PHMS, Nichimen Corp., Tokyo, Japan). Due to the two reactions a two-step mass loss of 13.7 % and 15.1 % is
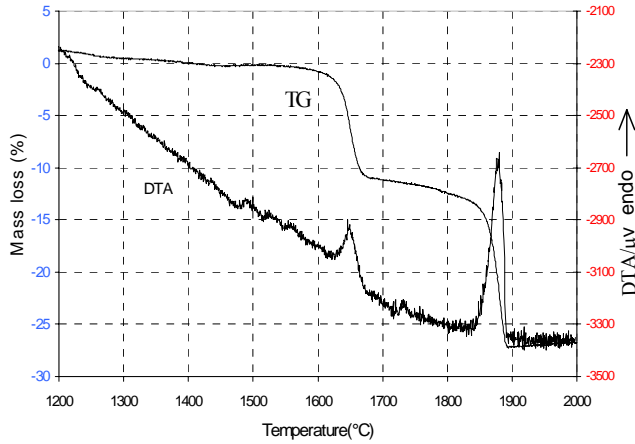

b) 2500 K

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Fig. 2. STA measurement for PHMS-derived ceramic; N_2-atmosphere, BN-crucible, 10K/min.
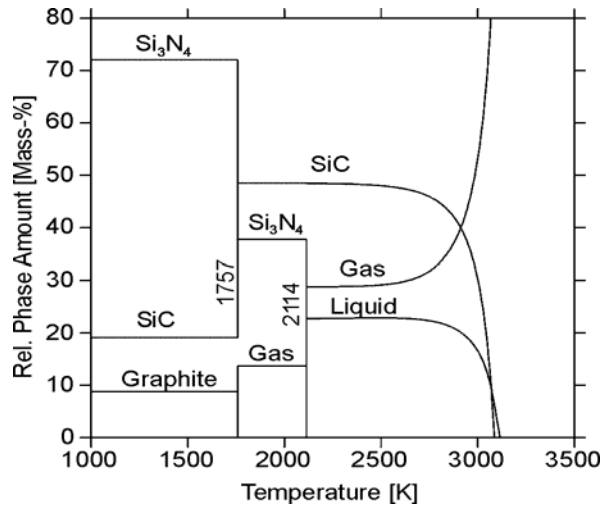

Fig. 3. Calculated phase fraction diagram in the Si-C-N system for PHMS-derived ceramics (C:Si < 1).

2.4 B-C-N System

The equilibrium diagram was calculated by extrapolation from the subsystems. Numerous metastable $B_xC_yN_z$ phases are described in this system.

2.5 Ti-Si-B System

So far this system was calculated by extrapolation from the binary subsystems. However, recently, a ternary phase Ti_6Si_2B was found [11] and a new ternary dataset has to be developed.

2.6 Ti-Si-C System

A thermodynamic dataset was developed by Du et al. [3] taking into account the solubility of carbon in the Nowotny phase Ti_5Si_3 and the ternary phase Ti_3SiC_2.

2.7 Ti-Si-N System

The Ti-Si-N system has been calculated by Seifert [12] taking into account the solubility of nitrogen in the Nowotny phase Ti_5Si_3.

2.8 Ti-B-C System

A thermodynamic dataset for this system was presented by Duschanek et al. [13]. Additional calculations in the system using this dataset were presented by Rogl and Bittermann [14].

2.9 Ti-B-N System

Thermodynamic calculations in the Ti-B-N system were presented by Groebner and Rogl [15]. The ternary system can be calculated from extrapolations from the binary subsystems.

2.10 Ti-C-N

Dumitrescu et al. [16] optimized the dataset by taking into account ternary experimental data. Ternary calculations were published [12].
TiN and TiC react with each other to form a complete solid solution of titaniumcarbonitrides according to the reaction:

$$xTiC+yTiN=Ti_{x+y}C_xN_y \text{ with } 0<x,y<1 \qquad (1)$$
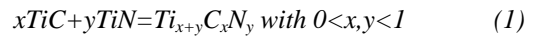
Alternatively, titaniumcarbonitrides can be synthesized by the reaction of TiN with carbon and the nitridation of TiC in N_2-atmosphere:

$$xTiC+y/2N_2=Ti_xC_{x-y}N_y+yC \text{ with } 0<x,y<1 \qquad (2)$$
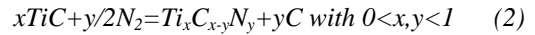
The specific composition of the resulting titaniumcarbonitride is a function of the sintering temperature and N_2-pressure. Additionally, titaniumcarbonitrides can be produced by heat treating titanium/carbon mixtures under N_2-atmosphere. Other methods used are the carbothermal reduction or self-propagating high-temperature synthesis. The reaction of TiC with N_2 was calculated as a function of temperature at N_2-pressures of 1 bar and 10 bar, respectively. The diagrams shown in Fig. 4 were derived assuming an arbitrary initial amount of 30 mol of atoms nitrogen (15 mol N_2) and 12 mol of atoms TiC.

3

The phase fraction diagrams give quantitative information on the reaction of TiC with the N_2 gas phase to form titaniumcarbonitride and graphite. Fig. 4a shows that the amount of N_2 decreases from 30 to 24 mol of atoms because at low temperatures (T<1250 K) the carbon component in TiC is almost totally exchanged by nitrogen and TiN and 6 moles of graphite are released. With increasing temperature more and more carbon remains in titaniumcarbonitride causing the increase of N_2 gas phase. Simultaneously the amount of released graphite decreases. The C:N ratio in the corresponding TiC_xN_{1-x} can be derived directly from Fig. 4b. The titaniumcarbonitride changes the composition from TiN (T<1250K) to $TiC_{0.87}N_{0.13}$ (1bar, 2500K) and $TiC_{0.67}N_{0.33}$ (10bar, T=2500K), respectively.

4a)
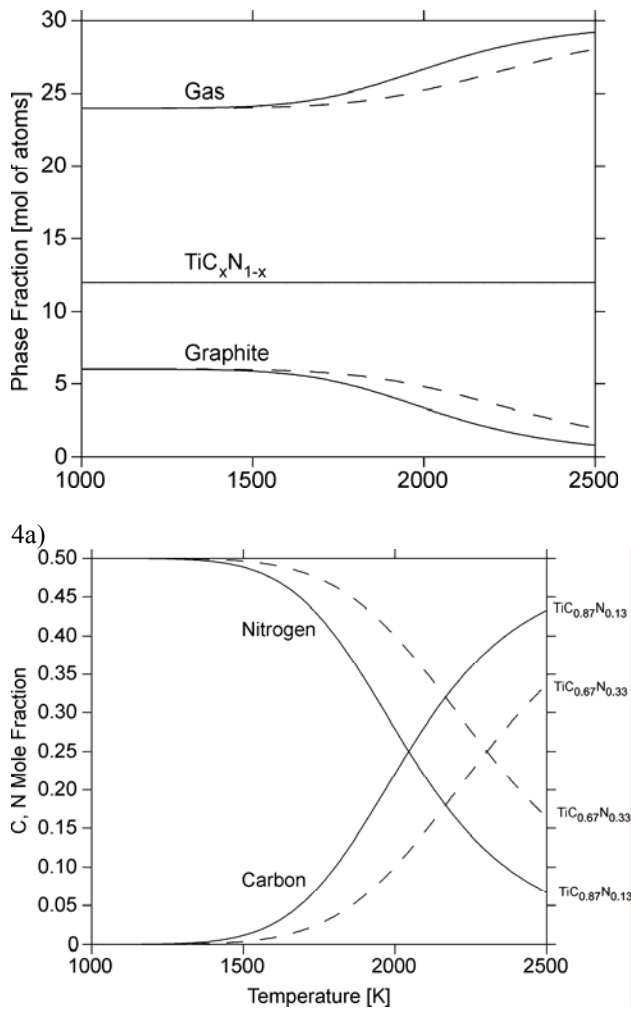
4 b)

Fig. 4. Calculated reactions of TiC with N_2 (p=1 bar, full lines; p=10 bar, dashed lines). a) Phase fraction diagram. b) Corresponding TiC_xN_{1-x} compositions.

3. QUATERNARY SYSTEMS

3.1 Si-B-C-N System

The incorporation of boron in Si-C-N ceramics can significantly increase their thermal stability. The XRD patterns of individual precursor-derived Si-B-C-N ceramics after DTA/TG with the highest temperature of 2200°C show that the material consists of Si_3N_4- and SiC-grains. The HRTEM images of these ceramics show Si_3N_4 grains "encapsulated" by a metastable matrix phase composed of BN and carbon with varying compositions (BNC_x). This effect increases the decomposition temperature of silicon nitride by an internal pressure increase. Ceramics with compositions in the center of the four-phase equilibrium Si_3N_4+SiC+BN+graphite and close to the three-phase equilibrium SiC+BN+graphite have shown to have this kind of microstructure and high temperature stability [17]. The potential phase diagram is shown in Fig. 5. The decomposition temperature of silicon nitride increases from 2114 K at 1 bar pressure to 2307 K at 10 bar pressure.
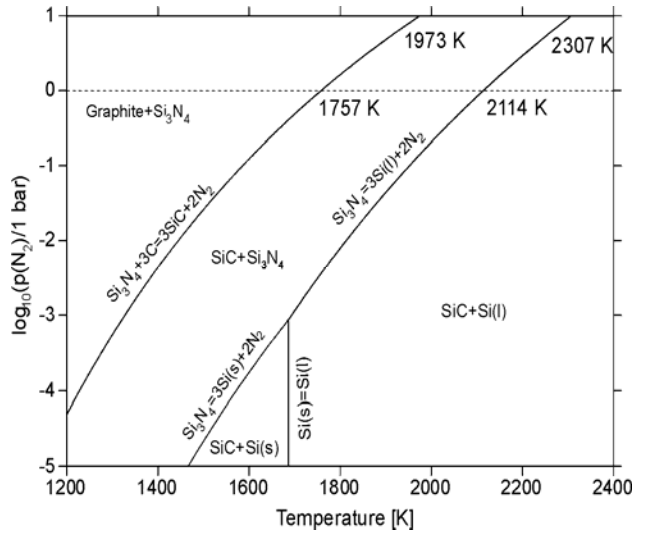

Fig. 5. Potential phase diagram in the Si-C-N system valid, for example, for PHMS-derived ceramics with C:Si <1.

It also can be expected that the activity of carbon in the turbostratic BNC_x matrix is lowered. This will increase the reaction temperature of silicon nitride with carbon (Fig. 6). The combined pressure increase/activity decrease affects the stability of silicon nitride significantly.
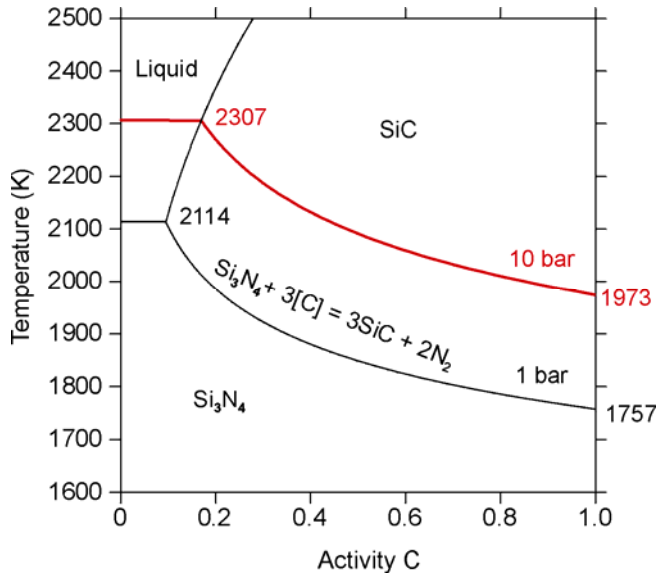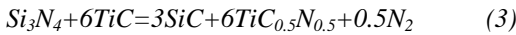
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Fig. 6. Temperature – carbon activity diagram in the Si-C-N system.

3.2 Ti-Si-C-N System

The phase reactions in this system were analyzed in detail [18,19].

Phase reactions of Si_3N_4 ceramics reinforced with TiC have been explained by the single chemical equation

$$Si_3N_4+6TiC=3SiC+6TiC_{0.5}N_{0.5}+0.5N_2 \qquad (3)$$

with a fixed initial Si_3N_4:TiC mol of atoms ratio of 7:12. This equation includes the assumption of a Si_3N_4-TiC mixture with 71.92 mass% TiC, which is much more than the usually introduced amount. Additionally, during sintering of these materials, the C:N ratio of the forming titaniumcarbonitrides is a function of the N_2-pressure and temperature, respectively, and may deviate significantly from a 1:1 ratio as assumed in equation (3).

The reactions of TiC with nitrogen become more complicated when TiC-Si_3N_4 mixtures are treated in nitrogen atmosphere. The reaction of Si_3N_4 with TiC in a mol of atoms ratio of 7:12 according to equation (3) is shown in Fig. 7a.

At temperatures lower than 1756 K Si_3N_4, Graphite, TiC_xN_{1-x} and N_2 gas are in equilibrium. At the temperature of 1756 K Si_3N_4 and free carbon react to form SiC (6 mol of atoms) and nitrogen gas. Some free carbon remains. Fig. 7b shows the corresponding composition of the titaniumcarbonitride as a function of the temperature. The composition changes similarly to the previously described reaction of TiC with N_2 (compare Fig. 4b. The equilibrium composition of titaniumcarbonitride at the reaction temperature of 1756

K is $TiC_{0.16}N_{0.84}$. At a temperature of 2045 K no more excess carbon exists to be incorporated in TiC_xN_{1-x}. The composition remains constant at $TiC_{0.5}N_{0.5}$. At temperatures higher than about 2300 K significant amounts of Si-containing gaseous species form, resulting in an increase of the carbon content in the titanium carbonitrides.

To compare phase reactions for different Si_3N_4:TiC ratios a further calculation for a mol of atoms ratio of 7:2 was carried out (Fig. 8).

At temperatures lower than 1756 K the phase equilibria are the same as in the previous case but with deviating phase fractions (compare to Fig. 7a). At a temperature of 1756 K Si_3N_4 and graphite react to form SiC and nitrogen gas (Fig. 8a). Additionally, titaniumcarbonitride of composition $TiC_{0.15}N_{0.85}$ (Fig. 8b) is found. In contrast to the material with a 7:12 mol of atoms ratio, at higher temperatures some Si_3N_4 remains stable together with SiC and TiC_xN_{1-x} and no graphite exists. At a temperature of 2113 K Si_3N_4 decomposes to form nitrogen and liquid silicon. The composition of the titaniumcarbonitride at this temperature is $TiC_{0.12}N_{0.88}$ (Fig. 8b). At higher temperatures the C:N ratio of the titaniumcarbonitride changes significantly.
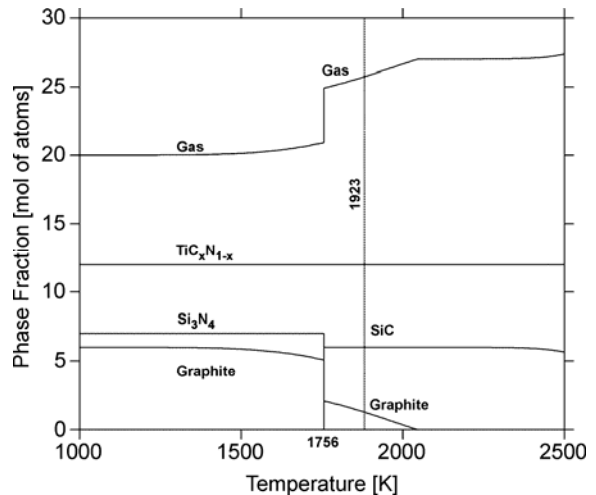

7a)

To determine the phase reactions of Si_3N_4 with variable amounts of TiC, calculations were carried out for a temperature of 1923 K, which is a typical sintering temperature for Si_3N_4-TiC materials. The initial Si_3N_4-fraction is fixed at 7 mol of atoms and the TiC fraction is continously increased. The result is shown in the phase fraction diagram (Fig. 9a).
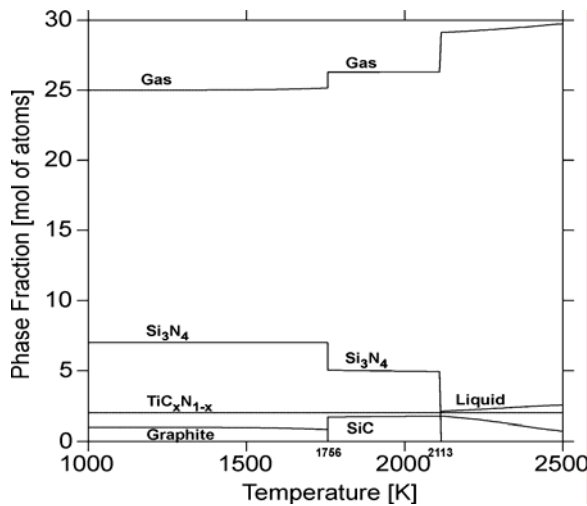
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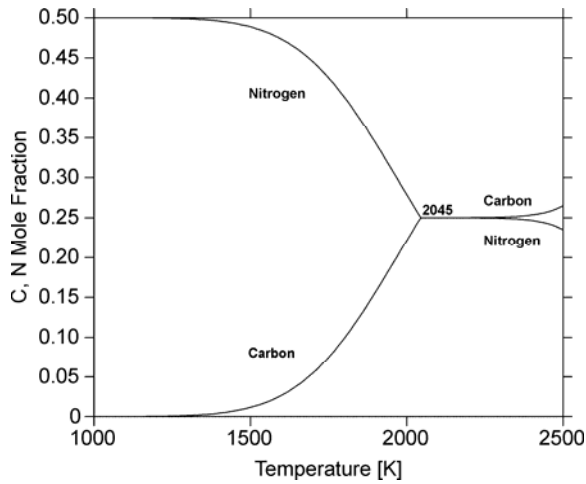
7b)

Fig. 7. Calculated reaction TiC with Si_3N_4 (mol of atoms ration 7:12) and N_2 (p=1bar). a) Phase fraction diagram. b) Corresponding TiC_xN_{1-x} compositions.
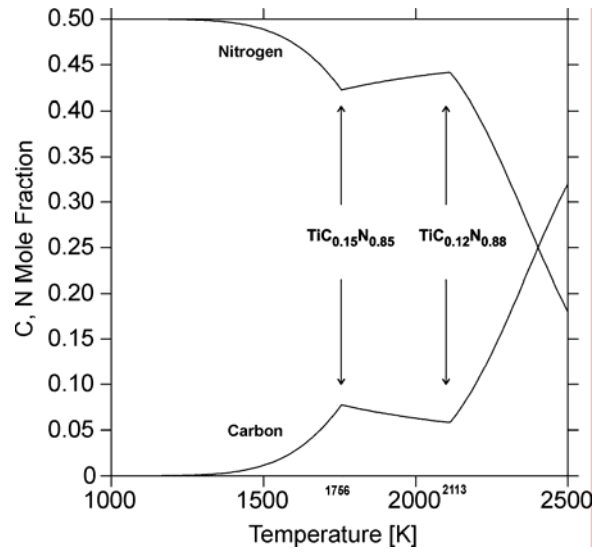
8b)

Fig. 8. Calculated reaction TiC with Si_3N_4 (mol of atoms ration 7:2) and N_2 (p=1bar). b) Corresponding TiC_xN_{1-x} compositions.

8a)

With increasing amount of TiC the Si_3N_4 fraction decreases with simultaneous formation of SiC and titaniumcarbonitride of composition $TiC_{0.13}N_{0.87}$ (Fig. 9b). This composition remains constant until all of the Si_3N_4 is used up. A higher input of TiC than 7 mol of atoms results in the formation of the three phase equilibrium titaniumcarbonitride, SiC and gas phase (not shown in the diagram). The composition of titaniumcarbonitride changes continously between $TiC_{0.13}N_{0.87}$ and $TiC_{0.34}N_{0.66}$. Adding more than 9 mol of atoms TiC free carbon is revealed (as graphite) and the titaniumcarbonitride composition remains constant at $TiC_{0.34}N_{0.66}$.

With changing temperatures and N_2-partial pressures the values will change but the general shape of the diagram remains.

The dashed lines in Figures 7a and 9a, respectively, indicate similar conditions (T=1923 K, Si_3N_4:TiC mol of atoms ratio 7:12).

A graphical representation of the previously calculated phase equilibria can be given by introducing reaction paths in the Ti-Si-C-N concentration tetrahedron (Fig. 10). The pure elements and the reacting ceramic compounds are indicated. The arrows indicate the reaction paths, originating on the Si_3N_4-TiC connecting line and end on tie triangles and tie lines, respectively. Two tie triangles are defined from the described calculations at a temperature of 1923 K: {1} $TiC_{0.34}N_{0.66}$+SiC+C and {3} $TiC_{0.13}N_{0.87}$+SiC+Si_3N_4. Two fields with two solid phases are defined: {2} TiC_xN_{1-x}+SiC (0.13<x<0.34) and {4} TiC_xN_{1-x}+Si_3N_4 (0<x<0.13). All solid phases are in equilibrium with nitrogen gas. Field {4} is not reached by reactions of Si_3N_4 and TiC and will be treated later.

Arrows pointing away from the nitrogen corner indicate a release of N_2 during the reaction of Si_3N_4 and TiC. Orientation towards the nitrogen corner indicate nitrogen consumption. At point A the connecting line Si_3N_4-TiC pushes through the tie triangle {1} $TiC_{0.34}N_{0.66}$+SiC+C. The arrow is shrinked to a point and no nitrogen is released or consumed from the atmosphere. According to these results, at selected physico-chemical conditions, the phase equilibria, the titaniumcarbonitride compositions and the reaction paths are a function of the Si_3N_4:TiC ratio only.
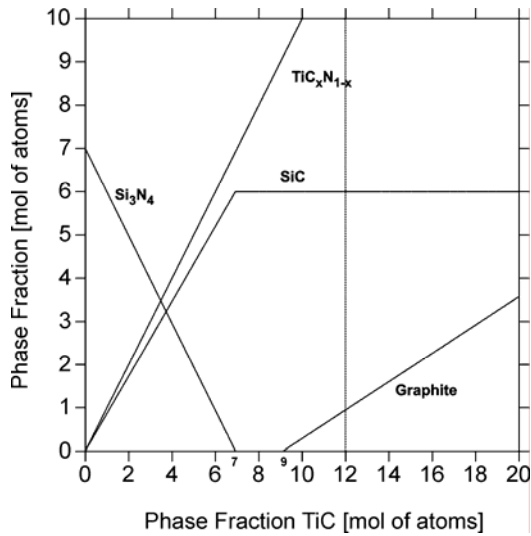
9a)
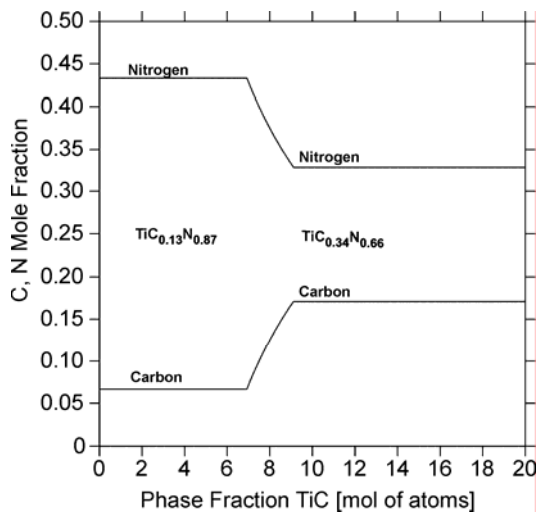
9b)

Fig. 9. Calculated reaction of Si_3N_4 with increasing TiC amount (1923 K, p=1bar). a) Phase fraction diagram. b) Corresponding TiC_xN_{1-x} compositions.

3.3 Ti-Si-B-C, Ti-Si-B-N and Ti-B-C-N Systems

These systems can be calculated by extrapolation. However, the recent detection of the new phase Ti_6Si_2B will require re-optimization.

CONCLUSIONS

Thermodynamic datasets for the binary, ternary and quaternary subsystems of the Ti-Si-B-C-N system are available. These data can be used for thermodynamic calculations in the quinary system. The thermodynamic dataset includes all refractory and hard materials of the system. High temperature reactions during military and commercial operation of components constructed from these materials can be simulated using the Ti-Si-B-C-N dataset. The recent detection of the Ti_6Si_2B phase in the

ternary Ti-Si-B system requires the optimization of this ternary system. Also, new thermodynamic datasets were recently published for the Ti-C [20] and the Si-N system [21]. These datasets have to be taken into account in future assessments.
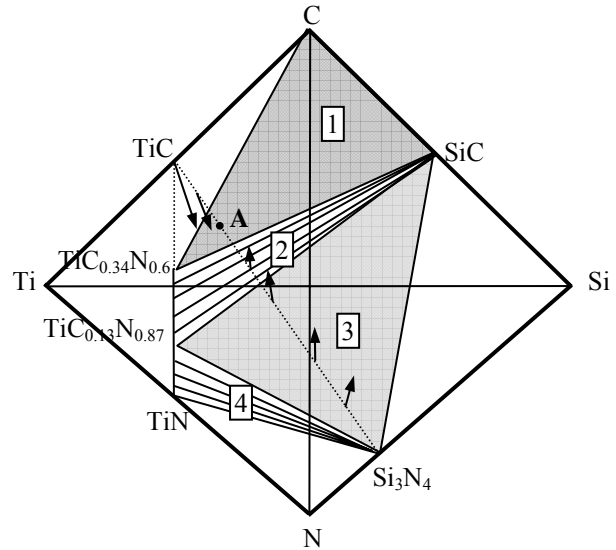

Fig. 10. Phase compatibilities with reaction paths for Si_3N_4-TiC mixtures at 1923 K.

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